

SINTERABLE NANOPOWDER CERAMIC MATERIAL AND METHOD FOR SYNTHESIS
THEREOF

The invention relates to a method of synthesizing a
5 multielement nanopowder that is directly suitable for sintering.
The invention also provides a multielement nanopowder and a
method of fabricating a $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramic in which the
above-mentioned multielement nanopowder is used.

$\text{Si}_3\text{N}_4/\text{SiC}$ structural composite ceramics present properties
10 such as high breaking strength, ability to withstand high
temperatures, and low density, that make them particularly
advantageous for applications involving thermal and mechanical
stresses, for example in the aerospace or automobile industries.
Nevertheless, the development of $\text{Si}_3\text{N}_4/\text{SiC}$ ceramics has been
15 hampered by the great difficulty involved in forming them. Such
forming requires a sintering step that generally needs to be
followed by a machining step that turns out to be lengthy,
difficult, and expensive because of the hardness of such
ceramics.

20 Sintering is commonly defined as high-temperature treatment
imparting mechanical cohesion to the sintered product: the
particles of the powder come closer together and weld to one
another, with the material densifying by a reduction in its
porosity and with linear shrinkage.

25 In practice, sintering a ceramic consists essentially in
heat treatment by heating the ceramic powder optionally in the
presence of sintering additives, and optionally accompanied by
said powder being compressed.

Sintering additives enable a liquid phase to appear at the
30 surfaces of the grains of powder, thereby leading to
densification of the ceramic.

For $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramics, it is known to use a
ceramic nanopowder containing silicon (Si), carbon (C), and
nitrogen (N), referred to as Si/C/N nanopowder, to make a slip

for the purpose of mixing said nanopowder with optionally nanometric sintering additives, generally Al_2O_3 and Y_2O_3 , to dry said slip, and to proceed finally with sintering. The step of mixing the nanopowder with sintering additives is nevertheless
5 always difficult, and the distribution of the additive is never uniform. Unfortunately, this poor distribution can lead to defects in the final ceramic, thereby degrading its properties.

In order to eliminate that critical mixing step, one solution is to incorporate the sintering additive elements
10 directly during the process of synthesizing the powder. To do that, a liquid mixture is made containing the elements Si, C, and N together with metal precursors comprising the sintering additive elements, e.g. aluminum (Al), oxygen (O), and yttrium (Y). An aerosol containing all of the above-mentioned elements
15 is then generated from the liquid mixture. The aerosol, mixed with a gas, is then sent through a laser beam and a Si/C/N/Al/Y/O multielement nanopowder is recovered, as produced during the interaction between the laser beam and the mixture. The interaction step is referred to as "laser pyrolysis".

Thus, it is known to synthesize Si/C/N/Al/O nanopowders
20 from a liquid mixture of hexamethyldisilazane $\text{Si}_2\text{C}_6\text{NH}_{19}$ (referred to below as HMDS), of isopropoxide $\text{C}_3\text{H}_7\text{OH}$, and of aluminum isopropoxide $\text{C}_9\text{H}_{21}\text{O}_3\text{Al}$, and also to synthesize Si/C/N/Al/Y/O nanopowders from a liquid mixture of HMDS, of isopropanol, of
25 aluminum isopropoxide, and of yttrium isopropoxide $\text{C}_9\text{H}_{21}\text{O}_3\text{Y}$. Those liquid mixtures are pulverized by means of an aerosol generator and they are injected into a reactor where they are subjected to laser pyrolysis. It should be observed that HMDS reacts slowly with isopropanol so it is necessary to subject the
30 mixture to treatment quickly once it has been made.

In that known method of synthesis, and in spite of the above-mentioned drawback, the presence of isopropanol is considered as being essential since it is believed that isopropanol favors solid isopropoxides dissolving in liquid

HMDS, and that it reduces the viscosity of the resulting liquid mixtures, thus making it possible firstly to obtain uniform nebulization of the mixture, and secondly to obtain a mixture that is suitable for being used in an aerosol generator, i.e. a liquid mixture of viscosity that is sufficiently low and containing the smallest possible amount of non-dissolved solid compounds.

An example nanopowder, written nanopowder B, obtained by that known method of synthesis is given in the last line of the TABLE below. Since the resulting nanopowder is essentially amorphous, its chemical composition is expressed in element percentages by weight, which corresponds to element analysis. On the basis of this composition in terms of element, a chemical composition expressed in terms of equivalent stoichiometric compounds is determined by calculation, as is common practice in the field of ceramics. This chemical composition expressed in terms of equivalent stoichiometric compounds is useful in practice for performing calculations and making comparisons, however at this step in the method of fabricating the ceramic, it does not reflect reality.

The list of equivalent stoichiometric compounds is given in the right-hand column of the TABLE below, and it was drawn up on the assumption that all of the atoms of Al and of Y are in the form of Al_2O_3 and Y_2O_3 , that the remaining atoms of oxygen are in the form of SiO_2 , and then that all of the atoms of nitrogen N are in the form of Si_3N_4 , and that the remaining atoms of Si are in the form of SiC; the excess free carbon atoms C_{free} are obtained by taking the difference between the total amount of carbon atoms and the amount of carbon atoms bonded with Si in SiC. This serves to determine the contents of sintering additives Al_2O_3 and Y_2O_3 , and also the contents of SiO_2 and C_{free} .

In the same manner as this example, nanopowders that have been obtained by previously-known methods of synthesis present high oxygen contents which lead to high SiO_2 contents and to high

carbon contents which lead to large C_{free} contents. Unfortunately, carbon inhibits densification of a nanopowder during sintering and is a source of defects, and thus of breaks in the resulting final ceramic. Furthermore, SiO_2 is harmful to the high-temperature mechanical properties of the ceramic.

Because of their composition, nanopowders synthesized using previously-known methods present very poor properties in terms of temperature stability (an average 30% loss of weight at 1500°C), so they must necessarily be subjected to an annealing step prior to sintering.

An object of the method of the invention is to synthesize a multielement nanopowder that is thermally stable and directly suitable for sintering, i.e. a nanopowder that is suitable for quickly reaching density close to the theoretical density of the ceramic that it is desired to obtain without it being necessary prior to sintering to perform a mixing step or an annealing step, and preferably without it being necessary to subject the powder to any heat treatment. The term "mixing step" is used to mean a step of mixing the nanopowder with sintering additives, as has been done conventionally in the past, e.g. using a slip.

To achieve this end, the invention provides a method of synthesizing a $\text{Si/C/N/E}_a/\text{F}_b/\text{G}_c/\text{O}$ multielement nanopowder directly suitable for sintering, where E, F, and G represent three distinct metallic elements other than Si, and at least one of a, b, and c is non-zero, the method comprising the following steps:

- using an aerosol generator to generate an aerosol comprising at least one metal precursor containing at least one of said metallic elements, and hexamethyldisilazane $\text{Si}_2\text{C}_6\text{NH}_{19}$ (HMDS) used as a main source of Si and as the sole solvent for said at least one metal precursor;
- adding to said aerosol silane SiH_4 or its equivalent in gaseous form so as to form a reaction mixture; and
- proceeding with laser pyrolysis of said reaction mixture.

It should be observed firstly that the $\text{Si/C/N/E}_a/\text{F}_b/\text{G}_c/\text{O}$ generic formula for the multielement nanopowder is not a stoichiometric formula and that the letters E, F, and G are selected arbitrarily to represent a plurality of possible
5 metallic elements. These three letters are therefore not chemical element symbols (unlike the letters C, Si, O, ... which are symbols for carbon, silicon, oxygen, ...).

Furthermore, throughout the present text, the indices a, b, and c serve solely to indicate the presence or the absence of
10 the corresponding metallic element. Thus, these indices can either be zero, or else non-zero, in which case they are equal to 1. Nevertheless, as specified, at least one of the indices must be non-zero. When an index is zero, that means that the nanopowder does not contain the corresponding element, and when
15 the index is non-zero (equal to 1), that means that the nanopowder contains the corresponding element. Thus, a $\text{Si/C/N/E}_a/\text{F}_b/\text{G}_c/\text{O}$ multielement nanopowder with non-zero a and zero b and c is a Si/C/N/E/O nanopowder that contains metallic element E, but contains neither F nor G.

In the method of the invention, no use is made of isopropanol, contrary to the technical prejudice which has been
20 to consider that isopropanol is necessary to ensure proper dissolution of the solid precursor in HMDS and to decrease the viscosity of the liquid mixtures used. HMDS is the sole solvent used for dissolving the metal precursor(s), regardless of
25 whether they are solid or liquid form, and against all expectations, the nanopowders synthesized by the inventors in the absence of isopropanol have shown that any solid precursors dissolve perfectly well in HMDS and that the viscosity of the
30 solutions obtained turns out to be sufficiently low for those solutions to be capable of being used in an aerosol generator.

In addition, the absence of isopropanol $\text{C}_3\text{H}_7\text{OH}$ presents the advantage of limiting the oxygen content and the carbon content within the synthesized nanopowder, such that the contents of SiO_2

and C_{free} are limited. By its very composition, the nanopowder therefore presents good temperature stability, and it is also directly suitable for sintering and can densify quickly.

Furthermore, adding silane SiH_4 , or its equivalent, as a
5 secondary source of silicon makes it possible to increase the Si content in the powder, thereby encouraging the formation of SiC from atoms of Si and excess carbon atoms, thus enabling the C_{free} content to be limited.

Furthermore, the Si-H bonds of the silane, or of its
10 equivalent, are effective absorbers of the radiation from the laser used for laser pyrolysis, thereby heating up the reaction mixture and enabling said mixture to be pyrolyzed at temperatures that are higher than they would be in the presence of HMDS without silane. Consequently, the decomposition of the
15 metal precursors is better, and the local order of atoms within the grains of synthesized nanopowder is improved thereby. Such an ordered structure leads in particular to grains having surfaces that are less sensitive to pollution by adsorbing O_2 and H_2O , thereby contributing to reducing the content of O in the
20 powder.

Thus, an equivalent of silane in the meaning of the invention is a compound comprising silicon and suitable for being used to increase the content of Si in the powder. In particular, as compounds that are equivalent to silane, mention
25 can be made of methylsilanes having the general formula $(\text{CH}_3)_{4-x}\text{SiH}_x$, chlorosilanes having the general formula $\text{Cl}_{4-x}\text{SiH}_x$, with $x=1, 2, \text{ or } 3$, and disilane Si_2H_6 .

Advantageously, said metallic elements E, F, and G are selected from the following metallic elements: aluminum (Al),
30 yttrium (Y), magnesium (Mg), ytterbium (Yb), and lanthanum (La). These elements are good sintering additive elements for composite ceramics of the $\text{Si}_3\text{N}_4/\text{SiC}$ type. It is preferable to select Al and Y as sintering metallic elements, or only one of those two elements.

As examples of metal precursors suitable for being used on their own or in combination, mention can be made of aluminum isopropoxide $C_9H_{21}O_3Al$, yttrium isopropoxide $C_9H_{21}O_3Y$, ytterbium isopropoxide $C_9H_{21}O_3Yb$, and aluminum secbutoxide $C_{12}H_{21}O_3Al$.

5 In a particular implementation of the method of the invention, ammonia NH_3 , or its equivalent, is added to said aerosol in gaseous form. This addition of ammonia can serve to increase the nitrogen content in the powder. By acting on the added ammonia NH_3 and silane SiH_4 used in forming said reaction
10 mixture, it is possible to vary the proportions of nitrogen and silicon in the powder, and for example to adjust the content of Si_3N_4 , which has an influence on the mechanical properties of the final ceramic.

In the meaning of the invention, ammonia equivalents are
15 gases containing nitrogen and suitable for being used to increase the nitrogen content in the powder. In particular, as compounds equivalent to ammonia, mention can be made of molecular nitrogen N_2 , methylamine CH_3NH_2 , and nitrogen protoxide N_2O .

20 The invention also provides a $Si/C/N/E_a/F_b/G_c/O$ multielement nanopowder where E, F, and G represent three distinct metallic elements other than Si, and at least one of a, b, and c is non-zero, the nanopowder being suitable for being obtained by the method of synthesis of the invention and being characterized in
25 that it is directly suitable for sintering without being subjected to a prior mixing step or a prior annealing step, in that each nanopowder grain contains all of the elements Si, C, N, E_a , F_b , G_c , and O, and in that it presents a chemical composition expressed in terms of equivalent stoichiometric
30 compounds determined by calculation from element analysis, such that the free carbon C_{free} content thereof is less than 2% by weight and the silicon oxide SiO_2 content thereof is less than 10% by weight.

The characteristic whereby each nanopowder grain contains all of the elements Si, C, N, E_a, F_b, G_c, and O specifies clearly that the claimed nanopowder is a genuine multielement nanopowder. In the technical field of the invention, it sometimes happens that the term "X/Y/Z multielement nanopowder" is used abusively to describe a powder in which each grain does not contain all of the elements X, Y, and Z. It should also be observed that at present, numerous nanopowders synthesized by prior art methods are not multielement nanopowders in the meaning of the invention. A good distribution of the various elements in each grain, and in particular a good distribution of the sintering additive metallic elements (these elements being the above-mentioned, E, F, and G, it being recalled that only one or two of these elements need be present, depending on the values of the indices a, b, and c, as mentioned above), makes it possible to obtain a nanopowder that is suitable for being sintered directly, and consequently to obtain a ceramic that presents very few structural defects and thus presents good properties. In particular, the better the structure of the ceramic (i.e. defects are fewer, and the grains are fine and spherically shaped), the better the plastic deformation properties thereof and the easier it is to make ceramic parts with high precision, thereby limiting the machining step.

Advantageously, said metallic elements E, F, and G are selected from the following metallic elements: aluminum (Al), yttrium (Y), magnesium (Mg), ytterbium (Yb), and lanthanum (La).

Advantageously, the index c of G_c is zero, so the nanopowder contains only two sintering metallic elements E and F. Furthermore, the metallic elements E and F are respectively advantageously aluminum Al and yttrium Y. Good results are obtained using only these two elements (these results are specified below).

Advantageously, the chemical composition of the nanopowder expressed in terms of equivalent stoichiometric compounds, as determined by calculation from the chemical composition in terms

of elements, is such that the sum of the contents of Al_2O_3 and Y_2O_3 is greater than 3%. It is found that below this value, the nanopowder is more difficult to sinter.

The invention also provides the use of a $\text{Si/C/N/E}_a/\text{F}_b/\text{G}_c/\text{O}$ multielement nanopowder of the invention in fabricating a composite ceramic, and a method of fabricating a composite ceramic in which: a $\text{Si/C/N/E}_a/\text{F}_b/\text{G}_c/\text{O}$ multielement nanopowder that is directly suitable for sintering is synthesized using the synthesis method of the invention; and said nanopowder is sintered directly, i.e. without subjecting it to a prior mixing step or a prior annealing step (and preferably no other heat treatment either).

It is found that the $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramic obtained by the above-mentioned method differs from previously-known ceramics, in particular in the nanometric size of its grains. The invention thus also provides a composite ceramic of the $\text{Si}_3\text{N}_4/\text{SiC}$ type made from a $\text{Si/C/N/E}_a/\text{F}_b/\text{G}_c/\text{O}$ multielement nanopowder in which E, F, and G represent three distinct metallic elements other than Si, and in which at least one of a, b, and c is non-zero (i.e. equal to 1) and suitable for being obtained by the above-defined fabrication method, that is characterized by the fact that the grains constituting it are of nanometer size, i.e. less than 100 nanometers (nm).

The small size of the grains can make it possible in particular for the resulting $\text{Si}_3\text{N}_4/\text{SiC}$ ceramic to present good plasticity at high temperature, thereby making it easier to fabricate ceramic parts with good precision (e.g. by hot-forming) and to limit the machining step.

Advantageously, the $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramic of the invention presents density equal to 100% of its theoretical density. Such a density makes it possible, amongst other things, to guarantee good mechanical performance of the ceramic.

The invention can be well understood and its advantages will appear better on reading the following detailed description

of a particular implementation of the method of the invention,
of an example of a nanopowder of the invention, and of an
example of the use of said nanopowder to fabricate a composite
ceramic. The description refers to the accompanying drawings,
5 in which:

- Figure 1 is a section view of a "pyrosol" type liquid aerosol generator;

- Figure 2 is a section view of a reactor within which a reaction mixture crosses through a continuous wave CO₂ laser;

10 • Figure 3 shows concentration profiles (in percentages by weight) for each element in the nanopowder, obtained from one hundred different zones of a nanopowder compact of the invention;

15 • Figure 4 is a spectrum obtained by energy-dispersive spectrometry (EDS), as performed on a grain of the nanopowder of the invention; and

- Figure 5 is a curve showing the densification of a nanopowder of the invention.

20 With reference to Figures 1 and 2, there follows a description of a particular example of the method of synthesizing a Si/C/N/Al/Y/O nanopowder. The nanopowder is synthesized by laser pyrolysis of a reaction mixture, itself obtained by ultrasonic spraying of a liquid mixture comprising HMDS (liquid) and two metal precursors: aluminum secbutoxide
25 C₁₂H₂₁O₃Al (liquid), and yttrium isopropoxide C₉H₂₁O₃Y (salt dissolved in HMDS). In the present example, the liquid mixture was made up of 73.5% HMDS, 11.4% C₁₂H₂₁O₃Al, and 15.1% C₉H₂₁O₃Y. That mixture was suitable for spraying by means a commonly used "pyrosol" type aerosol generator, and without any particular
30 problem.

It should be observed that other types of aerosol generator could be used for implementing the method of synthesis of the invention, such as, for example, an injector type generator.

A "pyrosol" type aerosol generator is shown in Figure 1. It comprises a glass enclosure 2 fitted at its base with an ultrasound transducer 4. The transducer 4 is a piezoelectric pellet of barium titanate having a diameter of 40 millimeters (mm), tuned to a frequency of about 800 kilohertz (kHz). It is powered by a radiofrequency (RF) generator 6 delivering a power of 100 watts (W). The electrical oscillations are transformed by the transducer 4 into mechanical vibrations giving rise to ultrasound waves.

The above-specified liquid mixture is introduced into the glass enclosure 2 in the vicinity of the transducer 4 via a pipe 8. The ultrasound waves emitted by the transducer 4 propagate through the liquid mixture inducing a cavitation phenomenon in its subsurface zone. The cavities exploding at the surface of the liquid mixture lead to a thick mist of fine droplets being formed. The liquid aerosol as formed in this way is then entrained by an entraining gas introduced into the enclosure 2 via a pipe 10, so as to penetrate into a stainless steel reactor 12, as shown in Figure 2. The entraining gas comprises ammonium NH_3 , thus encouraging the formation of a nanopowder that is rich in nitrogen N.

In addition, gaseous silane SiH_4 , forming a secondary source of Si (the main source being the HMDS), is mixed with the liquid aerosol droplets to form a reaction mixture prior to the aerosol reaching the reaction zone situated at the center of the reactor 12. Inside the reactor 12, the pressure is controlled, as is the atmosphere which is constituted by argon. The reaction mixture is then injected along arrow E into the bottom portion of the reactor 12. The stream of reaction mixture 13 crosses through an infrared CO_2 laser 11 emitting at 10.6 micrometers (μm). The interaction between the laser and the reaction mixture gives rise to a flame 14. The nanopowder grains 15 are produced during the laser/mixture interaction, and are then transported in a stream of argon gas along arrow S towards a

collection chamber fitted with a filter. The nanopowder grains are collected in this chamber.

For a better understanding of certain steps in the above-described method, it should be observed that it can be advantageous to refer to two scientific publications dealing with synthesizing nanopowders by laser pyrolysis, and having the following references:

• R. Dez, F. Ténégat, C. Reynaud, M. Mayne, X. Armand, N. Herlin-Boime, Laser synthesis of silicon carbonitride powders, structure and thermal stability, Journal of the European Ceramic Society, 22 (2002), 2969-2979; and

• M. Cauchetier, X. Armand, N. Herlin, M. Mayne, S. Fusil, Si/C/N nanocomposite powders with Al (and Y) additives obtained by laser spray pyrolysis of organometallic compounds, Journal of Materials Science, 34 (1999), 1-8.

Once the nanopowder was recovered, the concentration profiles (in percentage by weight) of each element in the nanopowder were initially measured at one hundred different zones of a compact of the nanopowder. The concentrations were measured using an electronic microprobe or Castaing microprobe. Furthermore, a scanning electron microscope was used to take pictures of the nanopowder.

The concentration profiles are given in Figure 3. It can immediately be seen that the elements Al, Y, and O are indeed present throughout the nanopowder. It was observed that the density peaks correspond to grains that can be seen to be larger size in the microscope images.

These results were verified by energy-dispersive spectrometry (EDS) using a 10 nanometer (nm) nanoprobe serving to analyze the nanopowder grain by grain. Figure 4 shows one of the EDS spectra obtained from a single nanopowder grain. The spectrum conforms that all of the elements Si, C, N, Y, Al, and O are present within a single grain.

TABLE

	Composition in terms of elements (% by weight)							Composition in terms of equivalent compounds (% by weight)					
	Y	Al	Si	C	N	O	H	Y ₂ O ₃	Al ₂ O ₃	Si ₃ N ₄	SiC	SiO ₂	C _{free}
Nanopowder A	2.9	0.7	57.1	9.7	22.4	6.5	0.7	3.7	1.3	56.5	27.3	9.6	1.6
Nanopowder B	1.4	1.6	42.5	32.5	10.8	11.2	-	1.8	3.0	27.2	25.6	17.6	24.8

Above is a table giving the chemical composition in terms of elements and in terms of equivalent stoichiometric compounds for a nanopowder A obtained using the method of the invention as described above and for a nanopowder B obtained by a prior art method. The chemical compositions are given as percentages by weight.

It can clearly be seen from the table that the concentrations in SiO₂ and C_{free} are much lower in the nanopowder of the invention. These low concentrations associated with the presence of all of the elements, and in particular of the sintering additive elements (Al, Y, and O) on each grain of powder, have as a first consequence the fact that the resulting nanopowder presents better temperature stability than do previously-known nanopowders (similar to B). By measuring this stability by annealing under a nitrogen atmosphere, it is found that weight loss is less than 1% at 1500°C, whereas with prior nanopowders, weight loss at 1500°C is at least 20%. The second sequence of these low concentrations of SiO₂ and C_{free} is that the nanopowder of the invention can be sintered without being subjected to annealing.

The densification curve shown in Figure 5 was obtained by preparing a sample of the nanopowder of the invention, placing the sample in a mold, and subjecting it to sintering by uniaxial pressing (or high pressure (HP) sintering) at a pressure of 35 megapascals (MPa) with a temperature rise gradient of 20°C/min with a pause of 10 min at 1750°C. Under such

circumstances, density can be achieved that is not less than 99.5% of the theoretical density of the ceramic. A fully dense ceramic composite of the $\text{Si}_3\text{N}_4/\text{SiC}$ type can thus be obtained easily and quickly by sintering the nanopowder of the invention.

5 In a variant implementation of the method of fabricating a ceramic in accordance with the invention, the nanopowder can be sintered other than by uniaxial pressing: for example it is possible to use the well-known techniques of sintering by hot isostatic pressing (HIP) or by spark plasma sintering (SPS).

10 The good physical properties of $\text{Si}_3\text{N}_4/\text{SiC}$ type ceramics fabricated out of the nanopowder of the invention, such as high breaking strength, temperature stability, good ability to withstand thermal shock, and high toughness, make these ceramics particularly suitable for industrial applications involving
15 thermal and mechanical stresses. Thus, the ceramic can be used in making cutting tools or ball bearings. Furthermore, the low density of these ceramics (specific gravity substantially equal to 3.2) means that they can also be used for making parts in the automobile and aerospace fields, such as engine valves, valve
20 guides, or pistons and rotors for turbocompressors. The advantages of ceramics compared with metals are greater resistance to wear, reduction in friction forces, low coefficient of thermal expansion, low density, and the possibility of using them at higher temperatures.

25 Finally, the refractory capacity of the ceramics, their resistance to high temperatures, and their chemical stability against molten metals enable them to be used when casting aluminum, as casting tubes, casting dies, and pump rotors.

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